Working Group on Strategies and Review, Fiftieth session, 10-14 September 2012

# <u>Informal document</u> As supplementary information to draft guidance document ECE/EB.AIR/WG.5/2012/1

Provisional Agenda Item 4
Draft guidance document on best available techniques
for controlling emissions from heavy metals and
their compounds from the source categories listed in Annex II

### Draft guidance document, showing tracked changes to Annex III of the Protocol on Heavy Metals

#### **Summary**

As supplementary information to document ECE/EB.AIR/WG.5/2012/1 which contains the draft guidance document on best available techniques to the Protocol on Heavy Metals, this document shows in tracked changes the modifications made to Annex III of the Protocol on Heavy Metals. It is intended to facilitate delegates' consideration of the document at the session.

ANNEX III
BEST AVAILABLE TECHNIQUES FOR CONTROLLING
EMISSIONS OF HEAVY METALS AND THEIR COMPOUNDS FROM THE SOURCE
CATEGORIES LISTED IN ANNEX II
I. INTRODUCTION

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## **Economic Commission for Europe**

Executive Body for the Convention on Long-range Transboundary Air Pollution

# Working Group on Strategies and Review

### Fiftieth session

Geneva, 10–14 September 2012 Item 4 of the provisional agenda

Draft guidance document on best available techniques for controlling emissions of heavy metals and their compounds from the source categories listed in annex II

Draft guidance document on best available techniques for controlling emissions of heavy metals and their compounds from the source categories listed in annex II\*

### Note by the Chair of the Task Force on Heavy Metals

#### **Summary**

At its forty-ninth session in September 2011, the Working Group on Strategies and Review agreed that the Protocol on Heavy Metals should be made more adaptable to future developments through the production of a guidance document on best available techniques extracted from annex III to the Protocol (ECE/EB.AIR/WG.5/2011/19).

This note includes the draft guidance document as prepared by the Task Force on Heavy Metals, with due account of comments by Parties and other experts, as requested by the Working Group. Justifying remarks are provided in the Report of the Task Force on Heavy Metals on the Workshop to promote the ratification of the Protocol on Heavy Metals (ECE/EB.AIR/WG.5/2012/2).

Text in square brackets had not yet been discussed by the Working Group on Strategies and Review.

<sup>\*</sup> This note is being issued without formal editing.

# **List of abbreviations and acronyms**

ACI	Activated carbon injection
As	Arsenic
BAT	Best available techniques
<u>BF</u>	<u>Blast furnace</u>
BOF	Basic oxygen furnace
BREF <sup>1</sup>	Best available technique reference document
<u>CaBr<sub>2</sub></u>	Calcium bromide
Cd	Cadmium
<u>Cl<sub>2</sub></u>	<u>Chlorine</u>
Co	Cobalt
Cr	Chromium
Cu	Copper
Cu <sub>2</sub> HgI <sub>4</sub>	Copper(I) tetraiodomercurate (II)
cts/kWh	Cents per kilowatt hour
CFA	Circulating fluidized-bed absorber
EAF	Electric arc furnace
ECE	United Nations Economic Commission for Europe
ELV	Emission limit values
EMEP	European Monitoring and Evaluation Programme under the Convention on Long-Range
	Transboundary Air Pollution (LRTAP)
ESP	Electrostatic precipitator
FF	Fabric filter
FGD	Flue gas desulphurization
<u>HEPA</u>	High efficiency particulate air filter
<u>H</u> <sub>2</sub> O	Water
$\underline{\text{H}_2\text{SeO}_3}$	Selenious acid
Hg	Mercury
HgCl <sub>2</sub>	Mercuric chloride
Hg <sub>2</sub> Cl <sub>2</sub>	Mercury (I) chloride
Hg+	Mercury ion
HgO	Mercury oxid
HgSO <sub>4</sub>	Mercury (II) sulfate
$H_2SO_4$	Sulphuric acid
IGCC	Integrated gasification combined-cycle
K	Kelvin
<u>kPa</u>	Kilo pascal
kWel	Kilowatt electric

<sup>&</sup>lt;sup>1</sup> For latest reference documents giving information on all relevant sectors, techniques and processes used, current emission and consumption levels, BAT and emerging techniques: http://eippcb.jrc.es/reference/.

mg/l	Milligramme per litre
$\frac{\text{mg/r}}{\text{mg/m}^3}$	Milligramme per cubic metre
•	
mg/Nm <sup>3</sup>	Milligramme per normal cubic metre
mg/t	Milligramme per ton
Mg	Megagramme, metric ton
$\mu g/Nm^3$	Microgramme per normal cubic metre
Ni	Nickel Nickel
NO <sub>x</sub>	Nitrogen oxide
<u>O</u> <sub>2</sub>	Oxygen
Pb	Lead
PARCOM	Commission for the Prevention of Marine Pollution from Land-based Sources
PCDD/F	Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran
PM	Particulate matter
ppm	Parts per million
Sb	Antimony
SCR	Selective Catalytic Reduction
Se	Selenium
Sn	<u>Tin</u>
<u>SO<sub>2</sub></u>	Sulphur dioxide
TOC	Total organic carbon
UNEP	United Nations Environment Programme

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# I. Introduction

- 1. This guidance document aims to provide Parties with guidance on identifying best available techniques for stationary sources to enable them to meet the obligations of the Protocol.
- 2. "\_\_\_\_\_ The expression "Best available techniques" (BAT) means" identifies the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle—the basis for emission limit values (and other permit conditions) designed to prevent and, where that is not practicable, generally—to reduce emissions and their the impact on the environment as a whole:
- <u>"Techniques"</u> includes both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned; <u>"Available"</u>
- (b) "Available" techniques means those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the territory of the Party Member State in question, as long as they are reasonably accessible to the operator; "Best'
- (c) "Best" means most effective in achieving a high general level of protection of the environment as a whole. Criteria for determining BAT are as follows:

In determining the best available techniques, special consideration should be given, generally or in specific cases, to the factors below, bearing in mind the likely costs and benefits of a measure and the principles of precaution and prevention:

<u>-(i)</u> The low-waste technology; use The of less hazardous substances; The furthering of recovery and recycling of substances generated and used in process and -, where appropriate; (iv) Comparable processes, facilities or methods of operation which have been tried with industrial scale; success on an Technological advances and changes in scientific knowledge and understanding; The nature, effects volume the emissions concerned; and of The (vii) commissioning dates for new existing installations; (viii) The length of time needed to introduce the best available technique;

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- The consumption and nature of raw materials (including water) used in the process and its energy efficiency;
- The need to prevent or reduce to a minimum the overall impact of the emissions on the environment and the risks to it;

  The need to prevent accidents and to minimize their consequences for the environment.
- (xi) The need to prevent accidents and to minimize their consequences for the environment;
- (xii) Information published by national and international organizations.

The concept of best available techniques BAT is not aimed at the prescription of any specific technique or technology, but at taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions.

- 3.- The information regarding emission control performance and costs is based on official documentation of the Executive Body and its subsidiary bodies, in particular documents received and reviewed by the Task Force on Heavy Metal-Emissions and the Ad Hoc Preparatory Working Group on Heavy Metals. Furthermore, other international information on best available techniques for emission control has been taken into consideration (e.g. such as BAT reference documents from the European Community's Integrated Pollution Prevention and Control Bureau (EIPPCB), the UNEP 2002 Global Mercury Assessment, and various technical notes on BAT, reports from United States Environmental Protection Agency (U.S. EPA), Environment Canada, and the PARCOM recommendations for BAT, European Commission and information provided directly by experts). has been taken into consideration.
- 4.- Experience with new products and new plants incorporating low-emission techniques, as well as with the retrofitting of existing plants, is growing continuously; this annex guidance document may, therefore, need amending and updating.
- 5.- The annexguidance document lists a number of measures spanning a range of costs and efficiencies. The choice of measures for any particular case will depend on, and may be limited by, a number of factors, such as economic circumstances, technological infrastructure, any existing emission control device, safety, energy consumption and whether the source is a new or existing one.
- 6.- This annex guidance document takes into account the emissions of cadmium; (Cd), lead (Pb) and mercury (Hg) and their compounds, in solid (particle-bound) and/or gaseous form. Speciation of these compounds is, in general, not considered here. Nevertheless, the efficiency of emission control devices with regard to the physical properties of the heavy metal, especially in the case of mercury, has been taken into account.
- 7.- Emission values expressed as mg/m³ refer to standard conditions (volume at 273.15 K, 101.3 kPa, dry gas) not corrected for oxygen content unless otherwise specified, and are calculated in accordance with draft CEN (Comité <u>européenEuropéen</u> de <u>normalisation</u>) and, in some cases, national sampling and monitoring techniques.

H. GENERAL OPTIONS FOR REDUCING EMISSIONS OF HEAVY METALS AND THEIR COMPOUNDS

# II. General options for reducing emissions of heavy metals and their compounds

- 8.- There are several possibilities for controlling or preventing heavy metal emissions.- Emission reduction measures focus on add-on technologies and process modifications (including maintenance and operating control).- The following measures, which may be implemented depending on the wider technical and/or economic conditions, are available:
- (a)-\_\_\_Application of low-emission process technologies, in particular in new installations;
- (b) \_\_Off-gas cleaning (secondary reduction measures) with filters, scrubbers, absorbers, etc.;
- (c) \_\_\_Change or preparation of raw materials, fuels and/or other feed materials (e.g. use of raw materials with low heavy metal content);
- (d) \_\_\_Best management practices such as good housekeeping, preventive maintenance programmes, or primary measures such as the enclosure of dust-creating units;
- (e)\_\_\_\_ Appropriate environmental management techniques for the use and disposal of certain products containing Cd, Pb, and/or Hg.
- 9.- It is necessary to monitor abatement procedures to ensure that appropriate control measures and practices are properly implemented and achieve an effective emission reduction.- Monitoring abatement procedures will include:
- (a)-\_\_\_Developing an inventory of those reduction measures identified above that have already been implemented;
- (b)-\_\_Comparing actual reductions in Cd, Pb and Hg emissions with the objectives of the Protocol;
- (c)-\_\_\_Characterizing quantified emissions of Cd, Pb and Hg from relevant sources with appropriate techniques;
- (d)-\_\_Regulatory authorities periodically auditing abatement measures to ensure their continued efficient operation.
- 10.- Emission reduction measures should be cost-efficient.- Cost-efficient strategy considerations should be based on total costs per year per unit abated (including capital and operating costs).- Emission reduction costs should also be considered with respect to the overall process.

# III. CONTROL TECHNIQUES Control techniques

- 11.- The major categories of available control techniques for Cd, Pb and Hg emission abatement are primary measures such as raw material and/or fuel substitution and low-emission process technologies, and secondary measures such as fugitive emissionemissions control and off-gas cleaning.- Sector-specific techniques are specified in chapter IV.
- 12.- The data on efficiency are derived from operating experience and are considered to reflect the capabilities of current installations.- The overall efficiency of flue gas and fugitive diffuse emission reductions depends to a great extent on the evacuation performance of the gas and dust collectors (e.g. suction hoods).- Capture/collection efficiencies of over 99% have been demonstrated.- In particular cases experience has shown that control measures are able to reduce overall emissions by 90% or more.

13.- In the case of particle-bound emissions of Cd, Pb and Hg, the metals can be captured by dust-cleaning devices.- Typical dust concentrations after gas cleaning with selected techniques are given in table 1.- Most of these measures have generally been applied across sectors.- The minimum expected performance of selected techniques for capturing gaseous mercury is outlined in table 2.- The degree of mercury control shown in this table is largely dependent on the chemical state and form of the mercury (e.g., oxidized, elemental or particle bound). The application of these measures depends on the specific processes and is most relevant if concentrations of mercury in the flue gas are high.

Table 1:
Performance of dust-cleaning devices expressed as hourly average dust concentrations

-Dust-cleaning devices	Dust concentrations after cleaning $\frac{2}{3}$ (mg/m <sup>3</sup> )	
Fabric filters	<del>&lt;10</del>	
Fabric filters, membrane type	< 1 <u>- 5</u> < <del>50</del> 1	
Dry electrostatic precipitators	< <del>50</del> 5 – 15 < <del>50 –</del> 1- 5	
Wet electrostatic precipitators	<pre>&lt; 20 0.1 - 1</pre>	
High-efficiency scrubbers		
Ceramic filters		

 $\it Note:$  Medium- and low-pressure scrubbers and cyclones generally show lower dust removal efficiencies.

Table 2: Minimum expected performance of mercury separators expressed as hourly average mercury concentrations

-Mercury separator	Mercury content after cleaning (mg/m³)
Selenium filter-	
Selenium scrubber-	
Carbon filter-	
Sulphur impregnated carbon filter Carbon injection + dust separator-	< 0.01- < 0.2 < 0.01
Odda Norzink chloride process-	< 0.01 < 0.05
Lead sulphide process-	< 0.05 < 0.1— < 0.05-
Bolkem (Thiosulphate) process	< 0.1-
Injection of brominated activated Carbon+ dust separator	0.001

<sup>&</sup>lt;sup>2</sup>Report of the Task Force on Heavy Metals on Assessments of BAT and limit values, June 2006

- 14.- Care should be taken to ensure that these control techniques do not create other environmental problems. The choice of a specific process because of its low emission into the air should be avoided if it worsens the total environmental impact of the heavy metals' discharge, e.g. due to more water pollution from liquid effluents. The fate of captured dust as well as of mercury-charged activated carbon resulting from improved gas cleaning must also be taken into consideration. A negative environmental impact from the handling of such wastes will reduce the gain from lower process dust and fume emissions into the air. Studies by the U.S. EPA show that the mercury is well-captured on the activated carbon and does not leach, e.g. from landfills.
- 15.- Emission reduction measures can focus on process techniques as well as on- off-gas cleaning.- The two are not independent of each other; the choice of a specific process might exclude some gas-cleaning methods.
- 16.- The choice of a control technique will depend on such parameters as the pollutant concentration and/or speciation in the raw gas, the gas volume flow, the gas temperature, and others.- Therefore, the fields of application may overlap; in that case, the most appropriate technique must be selected according to case- specific conditions.
- 17.- Adequate measures to reduce stack gas emissions in various sectors are described below.- Fugitive emissions have to be taken into account.- Dust emission control associated with the discharging, handling, and stockpiling of raw materials or by-products, although not relevant to long-range transport, may be important for the local environment.- The emissions can be reduced by moving these activities to completely enclosed buildings, which may be equipped with ventilation and dedusting facilities, spray systems or other suitable controls.- When stockpiling in unroofed areas, the material surface should be otherwise protected against wind entrainment.- Stockpiling areas and roads should be kept clean.
- 18.- The investment/cost figures listed in the tables have been collected from various sources and are highly case-specific. They are expressed in 1990 US\$ (US\$ 1 (1990) = ECU 0.8 (1990)). They depend on such factors as plant capacity, removal efficiency and raw gas concentration, type of technology, and the choice of new installations as opposed to retrofitting.

### IV. Sectors

19. This chapter contains a table per relevant sector with the main emission sources, control measures based on the best available techniques, their specific reduction efficiency and the related costs, where available. Unless stated otherwise, the reduction efficiencies in the tables refer to direct stack gas emissions.

# A. Combustion of fossil fuels in utility and industrial boilers (annex II, category 1)

- 20. The combustion of coal in utility and industrial boilers is a major source of anthropogenic mercury emissions.- The heavy metal content is normally several orders of magnitude higher in coal than in oil or natural gas. Fuel switching is sometimes an option if fuels with a lower mercury content are available (e.g. natural gas or specific types of coal with lower mercury content).
- 21. Improved energy conversion efficiency and energy conservation measures will result in a decline in the emissions of heavy metals because of reduced fuel

requirements.- Combusting natural gas or alternative fuels with a low lower heavy metal content instead of coal would also result in a significant reduction in heavy metal emissions such as mercury.—and can be regarded as one form of BAT. Integrated gasification combined-cycle (IGCC) power plant technology is a new planthigh efficiency technology with a low emission potential that can have reduced emissions compared to large scale power production based on solid fuels that do not use IGCC.

- 22. With the exception of mercury, heavy metals are <u>mostly</u> emitted in solid form in association with fly-ash particles. <u>Different coal combustion technologies show different magnitudes Therefore, BAT to reduce the emissions of fly ash generation: grate-firing boilers 20-40%; fluidized bed combustion 15%; dry bottom boilers (pulverized coal combustion) 70-100% of total ash. The heavy metal content in the small particle size fraction of metals is generally the fly ash has been found to be higher. application of high performance dedusting devices such as electrostatic precipitators (ESP) or fabric filters (FF).</u>
- 23. Beneficiation, e.g. "washing" or "bio-treatment", of coal reduces the heavy metal content associated with the inorganic matter in the coal—but is connected with emissions of heavy metals to water. However, the degree of heavy metal removal with this technology varies widely. Furthermore, the addition of halogens (especially bromides) to the fuel can promote the oxidation to less volatile mercury compounds, which can be removed in the ESP and flue gas desulphurization (FGD).
- 24. A For the combustion of coal and lignite, of liquid fuels and of biomass and peat a total dust removal of more than 99.5% can be obtained with electrostatic precipitators (ESP) (dust reduction rate > 99.5%) or fabric filters (FF), achieving dust concentrations of about (dust reduction rate > 99.95%). ESP and FF are both considered as BAT with daily average values for the concentration of dust in the range of below 5 up to 20 mg/m³ in many cases. m³) (referred to a flue gas oxygen content of 6%). When operated with well and continuously maintained equipment large coal fired power plants fitted with ESP or FF can achieve yearly average values of < 5 mg/m³. With the exception of mercury, heavy metal emissions can be reduced by at least 90-99%,% using an ESP or FF, the lower figure for the more easily volatilized elements.-
- 25. Mercury is at least partly and up to 90% present in the vapour phase and its collection by dust control devices is highly variable. Low filter temperature helps to reduce the gaseous mercury off-gas content. By injecting chemically-treated activated carbon, e.g. brominated, into the flue gas stream prior to the ESP or FF, mercury and mercury salts can be abated by more than 90% (Hg concentration  $< 1~\mu g/Nm^3$ ) and be taken out with the fly ash.
- 25 26. The application of techniques to reduce emissions of nitrogen oxides, by selective catalytic reduction (SCR) in combination with removal of sulphur dioxide and particulates from the flue gas can also remove heavy metals. Possible cross media impact should be avoided by appropriate waste water treatment.
  - 26. Using the For ESP or FF operated in combination with wet FGD techniques mentioned above, mercury removal efficiencies vary extensively from plant to plant, as seen in table 3. Research is ongoing to develop mercury, an average removal techniques, but until such techniques rate of 75% for Hg can be obtained, for certain coals, and/or if an adequate amount of oxidizing agent (e.g. halogens) are available on an industrial scale, nopresent in the flue gas. If a high dust SCR device is added upstream of the FGD an average removal rate of 90% can be obtained for Hg as long as adequate amounts of halogens are present in the flue gas (e.g., naturally present chlorine or added bromine). The best available technique is identified for the specific purpose of

removing mercurylevels of mercury control are generally achieved by emission control systems (e.g. SCR, FGD plus particulate control device) that use FF. The capture of mercury can be enhanced by injecting (chemically treated) activated carbon or adding other oxidizing compounds into the flue gas upstream of the ESP or FF or by distributing the flue gas throughout a carbon filter bed, except for high-volume combustion sources.

- 27. The least costly retrofit options for the control of Hg emissions from units with ESP or FF are believed to include:
- (a) Modification of dry FGD systems by the use of appropriate sorbents for the capture of Hg;
  - (b) Injection of a sorbent upstream of the ESP or FF;
- (c) Injection of a sorbent between the ESP and a pulse-jet FF retrofitted downstream of the ESP;
- (d) Installation of a semi-dry circulating fluidized-bed absorber (CFA) upstream of an existing ESP used in conjunction with sorbent injection.

The wet scrubber efficiency for mercury removal can be increased by:

- (e) Improving the liquid-to-gas ratio;
- (f) Wet FGD tower design. Research has shown that tray tower or open spray tower designs are effective in removing oxidized mercury from boiler flue gas;
- (g) Injection of activated carbon impregnated with additives (e.g. sulphur, bromine) increasing adsorption capacity;
  - (h) Increasing the ratio of oxidized mercury by:
  - (i) Addition of SCR device upstream of the wet scrubber;
  - (ii) Pre-treating coal (e.g. calcium bromide (CaBr2)).
- 28. The most cost-effective approach to control mercury emission from large combustion plants is an integrated multi-pollutant ( $SO_{2x}$ , NOx, PM, and Hg) control technology. By applying a combination of SCR, FGD and ESP or FF, the concentration of mercury (gaseous and solid) in the flue gases can be reduced to levels below 0.003 mg/m<sup>3</sup> as daily average at 6%  $O_2$ , A gas-phase oxidation process to simultaneously capture  $SO_{Xx}$ ,  $NO_{Xx}$ , and Hg is under demonstration.

Table 3:

Control measures, reduction efficiencies and costs for fossil-fuel combustion emissions

Emission source	Control measure(s)	Reduction efficiency (%)	<u>abat</u>	atement Indicative ement costs el costs US\$)	
Combo	Switch fuel	<del>oil to gas</del>	Cd, Pd: 100; Hg: 70-80	Highly case specific	
Combustio n of coal All fuels	Switch from coal to fuels with lower heavy metals emissions	Dust 70100_5	Highly case-sp	ecific	
	Coal cleaning	Cd, Pb: up to 80; <sup>4</sup> Hg <sup>a</sup> : 10 – 50			
	ESP (cold-side)	Cd, Pb: >-90;	Specific invest waste gas per h	ment US\$ 5-10/\textit{\textit{m}}^3 \textit{m}^3 \text{nour}	

Emission source	Control measure(s)	Reduction efficiency (%)	Abatement Indicative abatement costs (total costs US\$)
		Hg_a: 1040_5 PM: >99.5 - 99.8 4	$(> 200,000  \text{m}^4 / \underline{\text{m}}^3 / \underline{\text{h}})^5$
	(Wet fuel) flue-gas desulphurization (FGD) <sup>2/1</sup>	Cd, Pb: > 90; $\underline{5}$ Hg: $\frac{10-90}{5}$ b <sup>f</sup> : $\frac{30-70^{2}}{5}$ and $\frac{4}{5}$	15-30/Mg waste_gas <sup>5</sup>
	Fabric filters (FF)	Cd: >95; <sup>5</sup> Pb: >-99; <sup>5</sup> Hg <sup>b</sup> : 1060 <sup>5</sup> PM >99.95 <sup>4</sup>	Specific investment US\$8-15/ $\mathbb{m}^3$ m³ waste gas per hour (> 200,000 $\mathbb{m}^3$ / $\mathbb{m}^3$ /h) $\mathbb{m}^5$
	ESP or FF, and FGD	Hg <sup>b</sup> : 75 (average) <sup>6</sup>	0.03 - 0.15 US\$ cts/kWh <sup>7</sup>
	ESP or FF, and sorbent injection	<u>Hg: 50 – &gt;95</u>	90 % control: US\$ 35,000 – 70,000 per pound Hg removed (0.0003 – 0.002 US\$/kWh <sup>4</sup>
	Injection of (brominated) activated carbon (ACI)	<u>Hg: &gt;90</u>	US\$ 15,000 per pound Hg removed/ 0.0012 It kWh (ACI only)/ $6 - 30$ Mio. € per installatio 0.0001€ per k Wh); $1 - 2$ Mio US\$ per installation $\frac{9}{5}$ ; 0.0005 $- 0.003$ US\$/ kWh $\frac{10}{5}$
	ESP or FF, and carbon filter bed	<u>Hg: 80 – 90 <sup>4</sup></u>	<u>US\$ 33,000 – 38,000 per pound Hg removed</u>
	ESP or FF, and FGD and SCR (multi-pollutant approach)	Hg: 90 (average) <sup>4</sup> Hg: 30 – 70 for sub-bituminous coal and lignite <sup>7</sup>	No additional costs for Hg reduction based of multi-pollutant approach for $SO_2$ and $NO_x^{-3}$

<sup>-</sup>a/ Dependent on the type of coal used

## **Notes and References**

- 1. Hg removal efficiencies increase with the proportion of ionic mercury.- High-dust selective eatalytic reduction (SCR) installations facilitate Hg(II) formation.
- <u>b/</u>Removal can be facilitated by having adequate halogens present in the flue gas.
- 2. This <u>efficiency</u> is primarily for SO<sub>2</sub> reduction.- Reduction in heavy metal-emissions is a side benefit.- (Specific investment US\$ 60-250/kWel<del>.).</del> Wet scrubbers installed primarily for mercury cost between \$76,000 and \$174,000 per pound of mercury removed.
- 3. "Reduction of mercury emissions from coal fired power plants." Informal document no. 3, forty eighth session of the Working Group on Strategies and Review, 2011
- 4. "Assessments of technological developments: Best Available Techniques (BAT) and limit values." Draft background document for the third meeting of the Task Force Heavy Metals, April 2006
- 5. Heavy Metals Protocol 1998, Annex III
- 6. "Einstellung eines wissenschaftlichen Gutachtens zur Unterstuetzung des "Review der Technischen
- Anhaenge des UNECE Schwermetallprotokolls", O. Rentz et al, DFIU, November 2006
- 7. European Union BAT Reference document Large Combustion Plants, 2006
- 8. Fact sheets emission abatement techniques, infoMil 2009
- 9. Information provided by Albemarle
- 10. IPM Model Revisions to Cost and Performance for APC Technologies; Mercury Control Cost Development Methodology, Sargent & Lundy, Chicago, March 2011

<sup>&</sup>lt;sup>b</sup> Dependent upon the form of mercury present (HgO, Hg+)

### B. Primary iron and steel industry (annex II, category 2)

- This section deals with emissions from sinter plants, pellet plants, blast furnaces, and steelworks with a basic oxygen furnace (BOF). with subsequent casting. In integrated steelworks, sinter plants and steelworks dominate the overall emissions for most atmospheric pollutants including heavy metals. Emissions of Cd, Pb and Hg occur in association with particulates. dust. The content of the heavy metals of concern in the emitted dust depends on the composition of the raw materials and the types of alloying metals added in steel making. important. The most relevant emission reduction measures are outlined in table 4. Fabric filters FF should be used whenever possible; if conditions make this impossible, electrostatic precipitators ESP and/or high-efficiency scrubbers may be used.
  - 28. When using 30. The following techniques are considered as BAT in the:
  - (a) For sinter plants, BAT for dedusting of primary iron and steel industry, waste gas is to reduce dust emissions from sinter strand waste gas by means of a bag filter. For existing plants, if bag filters are not applicable, advanced ESP should be used. BAT for primary emissions from sinter strands is to prevent or reduce mercury emissions by selecting raw material with low mercury content or to treat waste gases in combination with activated carbon or activated lignite coke injection. A part of the waste gas should be recirculated if applicable in order to reduce the total waste gas as well as some other pollutants (e.g. NOx or PCDD/F). Please note that waste gas recycling does not affect the specific emission of dust directly related to the process can be reduced to emissions of heavy metals per ton of sinter. BAT for secondary emissions from sinter strand discharge, sinter crushing, cooling, screening and conveyer transfer points is to prevent dust emissions and/or to achieve an efficient extraction of dust emissions by using a combination of the following levels: techniques:

 Sinter plants	40 120 g/Mg
 Pellet plants	40 g/Mg
 Blast furnace	35 - 50 g/Mg
ROF	35 - 70 g/Mg
DOI	<del>- 55 /0 g/Mg.</del>

- 29. Purification of gases using fabric filters will
- (i) Hooding and/or enclosure;
- (ii) ESP or a bag filter;

The emissions level for mercury from sinter plants is < 0.03-0.05 mg/Nm<sup>3</sup>;

- (b) For pelletization plants, BAT is to reduce the dust content to emissions in the waste gases from the raw materials pre-treatment, drying, grinding, wetting, mixing and the balling; from the induration strand and from the pellet handling and screening by using one or a combination of the following techniques:
  - (i) ESP;
  - (ii) Bag filter;
  - (iii) Wet scrubber;
  - (c) For blast furnaces:
  - (i) BAT for casting house (tap holes, runners, torpedo ladles charging points, skimmers) is to prevent or reduce diffuse emissions by using the following techniques:
    - a. Covering the runners;

- Optimizing the capture efficiency for diffuse dust emissions and fumes with subsequent off-gas cleaning by means of an electrostatic precipitator or bag filter; Fume suppression using nitrogen while tapping, where applicable and where no collecting and de-dusting system for tapping emissions is installed; BAT is to minimize the release of blast furnace gas during charging by using one or a combination of the following techniques: Bell-less than 20 mg/m3, whereastop with primary and secondary equalizing; Gas or ventilation recovery system; For blast furnace gas cleaning BAT is to reduce dust emissions by using one or a combination of the following techniques: Dry pre-dedusting devices (such as deflectors, dust catchers, cyclones, ESP): Subsequent dust abatement (such as hurdle-type scrubbers, venture scrubbers, annular gap scrubbers, wet electrostatic precipitators, disintegrators); For basic oxygen furnace (BOF) plants: BAT for BOF gas recovery by suppressed combustion is to extract the BOF gas during blowing as much as possible and to clean it by using the following techniques in combination: Suppressed combustion process; Pre-dedusting to remove coarse dust by means of dry separation techniques (e.g. deflector, cyclone) or wet separators; Dust abatement by means of: Dry dedusting (e.g. ESP) for new and existing plants Wet dedusting (e.g. wet electrostatic precipitators or scrubber) for existing plants; BAT for BOF gas recovery during oxygen blowing in the case of full combustion is to reduce dust emissions by using one of the following techniques: Dry dedusting (e.g ESP or bag filter) for new and existing plants; b. Wet dedusting (e.g. wet ESP or scrubber) for existing plants. \_and scrubbers will reduce the dust content to 50 mg/m3 (as an hourlyBAT for secondary dedusting is to minimize dust emissions by means of process integrated techniques, such as general techniques to prevent or control diffuse or fugitive emissions, and by using appropriate enclosure and hoods with efficient extraction and a subsequent off-gas cleaning by means of a bag filter or an ESP or any other technique with the same
- (a) Reladling of hot metal from the torpedo ladle (or hot metal mixer) to the charging ladle;

removal efficiency. This applies also for the emissions from the following processes:

- (b) Hot metal pre-treatment (i.e. preheating of vessels, desulphurization, dephosphoristaion, deslagging, hot metal transfer processes and weighing);
- (c) BOF-related processes like the preheating of vessels, slopping during oxygen blowing, hot metal and scrap charging, tapping of liquid steel and slag from BOF;

(d) Secondary metallurgy and continuous casting.

For BOF plants the overall average). However, there are many applications of fabric filters in the primary iron and steel industry that can achieve much lower values. dust collection efficiency using BAT is well above 90%.

Table 4:Emission sources, control measures, dust reduction efficiencies and costs for the primary iron and steel\_industry

Emission source	Control measure(s)	Dust reduction efficiency (%)	Dust emission levels (mg/Nm³)	Abatement costs (total costs US\$)
Sinter plants primary emissions	Emission optimized sintering  Bag filters  Scrubbers and  ESP Advanced ESP (Moving Electrode ESP, ESP pulse system, high voltage ESP)	ca. 50 ≥ 99 > 90		<u></u> 3,000 – 16,000 €/a³
Sinter plants	Fabric Bag filters	<del>&gt; 99</del>	$\frac{\text{Hg:}}{< 0.03 - 0.05}$ $\frac{\text{mg/Nm}^3}{\text{m} < 10}$	
secondary emissions	ESP		< 30	
Pellet plants	ESP + lime reactor + fabric filters	> 99	<del></del>	<u></u>
	Scrubbers- <u>or semi-dry</u> <u>desulphurization and subsequent</u> <u>de-dusting</u>	> 95	<u> </u>	<u></u>
	Crushing, grinding, drying		<u>&lt; 20</u>	
	Other process steps		< 10- 15	
Blast furnaces	<del>FF /</del> ESP	> 99	< 10	ESP: 0.24-1/ <u>US\$/</u> Mg pig- <u>i</u> ron
Blast furnace	Wet scrubbers	> 99	<del></del> < 10	<u></u>
gas cleaning	Wet ESP	> 99	<del></del> <10	<u></u>
Blast furnace	Capture of diffuse emissions from the casting bay/cast house and subsequent dedusting by FF or ESP Diffuse emissions from casting bay/cast house		1–15	
BOF	Primary dedusting:  - dry ESP or FF  - wet separator/ESP/FF (existing plants)	> 99	10–30 < 50	Dry ESP: 2.25/ US\$/Mg steel
	Secondary dedusting: (including hot metal treatment and secondary metallurgy): dry ESP/FF	> 97	$\frac{< 20}{1-10}$	FF: 0.26 <del>/ US\$//</del> Mg steel
Fugitive	Closed conveyor belts,	80 – 99	<del></del>	

<sup>&</sup>lt;sup>3</sup> Report of the Task Force on Heavy Metals on Assessments of BAT and limit values, June2006

emissions	enclosure, wetting stored
CHIISSIONS	enclosure, wetting stored
	feedstock, cleaning of reads
	recustock, cleaning of reads

30

32. Direct reduction and direct smelting reduction are under development and proven alternative iron making processes to the coke oven/blast furnace route that may reduce the need for sinter plants and blast furnaces in the future. The application of these technologies depends on the ore characteristics and requires the resulting product to be processed in an electric arc furnace, which should be equipped with appropriate controls. As the heavy metals originate from the raw material, their emission levels are determined by the level of emission control (not by choice of process steps).

## C. Secondary iron and steel industry (annex II, category 3)

- 33. The secondary production of iron and steel 31. It is very important to capture all-mainly based on the use of Electric Arc Furnaces (EAF). BAT for EAF primary and secondary dedusting (including scrap preheating, charging, melting, tapping, ladle furnace and secondary metallurgy) is to achieve an efficient extraction of dust emissions efficiently. That is possible from all emission sources by installing doghouses or movable hoods or using one of the techniques listed below and to use subsequent dedusting by means of a FF:
  - (a) A combination of direct off-gas extraction and hood systems;
  - (b) Direct gas extraction and doghouse systems;
  - (c) <u>Direct gas extraction and total building evacuation.</u>

Ninety-eight per cent and more collection efficiency of primary and secondary emissions from EAF are achievable and considered as BAT. The captured emissions mustoff-gases can be eleaned. For all dust emitting processes in the secondary irontreated with activated carbon injection and steel industry, subsequent dedusting in by means of a fabric filtersfilter, which reduces the dust content to less than 20-5 mg/m3, shall be considered as BAT. When BAT is used also for minimizing fugitive emissions, the Nm³ and can achieve emission levels for mercury of < 0.05 mg/Nm³. The specific dust emissionemissions (including fugitive emission directly related to the process) will not exceed the range of between 0.1 to 0.6 and 0.35 kg/Mg steel. There are many examples of clean gas dust content below 10 mg/m³ when fabric filters

- 34. Mercury emissions can strongly vary from charge to charge depending on scrap composition/quality. Mercury emissions in the sector are used. The specific dust emission in expected to decline due to progressive phasing out of mercury following the full implementation of several directives and regulations in place, such eases is normally below 0.1 kg/Mg. as the 'End-of-Life Vehicles' Directive, the 'Waste from Electrical and Electronic Equipment' Directive as well as the 'Batteries' Directive in the European Union. For the melting of scrap, open-hearth furnaces are still in use, but are about to be phased out because of their inefficiency.
- 32. For the melting of scrap, two different types of furnace are in use: open-hearth furnaces and electric arc furnaces (EAF) where open hearth furnaces are about to be phased out.
  - 3335. The content of the heavy metals of concern in the emitted dust depends on the composition of the iron and steel scrap and the types of alloying metals added in steel-

making. steelmaking. Mercury emissions can strongly vary from charge to charge. Measurements at EAF have shown that 95% of emitted mercury and 25% of cadmium emissions occur as vapour. The most relevant dust emission reduction measures are outlined in table 5., which makes them difficult to capture. Exceedances of mercury ELVs have been observed, indicating that mercury bearing components still occur in scrap sources; emissions factors for mercury of 170 mg/t liquid steel (LS) could be detected. It is recommended as a best environmental practice to implement operating practices to prevent and minimize the presence of mercury and other heavy metals in the scrap, e.g. to remove mercury-bearing components prior to recycling in secondary iron and steel facilities. The most relevant dust emission reduction measures are outlined in table 5. Dust abatement techniques also provide for significant reductions of emissions of heavy metals. Gaseous lead and cadmium and its compounds as well as mercury that pass the dust filter can be abated by carbon adsorption, e.g. leading to 95% reduced emissions of mercury.

36. In recent years a number of new furnace types have been introduced, that might show advantages with regard to heavy metals and dust emissions, like the Comelt EAF and the Contiarc furnace.

Table 5:Emission sources, control measures, dust reduction efficiencies and costs for the secondary iron and steel industry

Emission source	Control measure(s)	Dust reduction Reduction efficiency		Abatement costs (total costs US\$)
EAF EAF	ESP ESP FF	≥ <u>99</u> > <del>99</del> ->99.5-	<u>Dust &lt; 5</u>	FF: 24/Mg steel-
	Activated c	<u>arbon</u> <u>Hg: &gt; 98%</u>	<u>Hg: &lt; 0.05</u>	

**Iron foundaries** (annex II, category 4)

#### 34. D. Iron and steel foundries

37. In the foundry process, emissions to air will typically not be limited to one (or several) fixed point(s). The process involves various emission sources (e.g. from melting and pouring processes). It is very important to capture all the emissions efficiently. That is possible by installing doghouses or movable hoods or by total building evacuation. The captured emissions must be cleaned. In iron foundries, cupola furnaces, electric arc furnaces—and, induction furnaces, hearth type furnaces and rotary furnaces are operated. Direct particulate and gaseous heavy metal emissions are especiallyin particular associated with melting and sometimes, to a small extent, with pouring. Fugitive Diffuse emissions arise from raw material handling, melting, pouring and fettling. The most relevant emission reduction measures are outlined in table 6 with their achievable reduction efficiencies and costs, where available. These measures The BAT associated emission level for dust, after collecting and dedusting exhaust gases, for all types of furnaces (cupola,

<sup>&</sup>lt;sup>4</sup> Reported by a Norwegian member of the technical working group on iron and steel of the European Union, 2008.

induction, and rotary furnace) and mouldings (lost mould and permanent mould) as well as finishing operations is 5–20 mg/m³.

- 38. The following techniques are considered as BAT:
- (a) For cupola furnace melting, use divided blast operation for cold blast cupolas, use oxygen enrichment of the blast air with oxygen levels between 22 and 25 %, minimize the blast-off periods for hot blast cupolas, use coke with known properties and of a controlled quality, and clean furnace off-gas using a bag filter or wet scrubber;
- (b) For induction furnace melting, increase furnace efficiency, maximize off-gas collection during the full working cycle, and use dry flue-gas cleaning keeping dust emissions below 0.2 kg/tonne molten iron;
- (c) For rotary furnace melting, optimize furnace operation and increase the melting efficiency. To collect the off-gas close to the furnace exit, apply post combustion, cool it using a heat ex-changer and to apply dry dedusting;
- (d) For electric arc furnaces a shortening of melt down times can be achieved by a close control of the composition (e.g. total content of phosphorus, sulphur and carbon), temperature control and efficient methods of deslagging. The foamy slag practice reduces the energy consumption and therefore the amount of exhaust gases;
- (e) For hearth type furnaces the use of oxyburners can reduce dust concentrations to 20 mg/m<sup>3</sup>, or less. the amount of energy necessary (e.g. gas or oil) for smelting of iron and therefore the total flow of exhaust gases;
- 35. The iron foundry industry comprises a very wide range of process sites. For existing smaller installations, the measures listed may not be BAT if they are not economically viable.
  - (f) For moulding, enclose all the unit operations and to dedust the exhaust gas, if necessary post combustion;
  - (g) For finishing operations, BAT is to collect and treat the finishing off-gas using a dry system.

Table 6:—
Emission sources, control measures, dust reduction efficiencies and costs for iron foundries

Emission source furnace	Control measure(s)	Dust reduction efficiency (%)	Abatement costs (total costs US\$) Emission levels (mg/Nm³)
EAF	ESP	<del>&gt; 99</del>	<del></del>
Induction furnace			FF: 24/Mg
	FF/dry absorption + FF <b>FF</b>	> 99 <del>.5</del>	iron <u>&lt; 5</u>
Cold blast cupola	Below-the-door take-off: FF	> <del>99</del> 98	<del></del>
	Below Above the door take	0007	
	off: FF + pre-dedusting	> <del>98</del> 97	<del></del>
-	Above-the-door take- off:-	> <del>97</del> 99	8-12/Mg iron
	FF + pre-dedustingFF		
	+ chemisorption		
Hot blast cupola	FF + chemisorptionpre-		
	dedusting	> 99	45/Mg iron

Emission source furnace	Control measure(s) <del>ESP</del>	Dust reduction efficiency (%) > <del>YY</del>	Abatement costs (total costs US\$) Emission levels (mg/Nm³)
Electric Arc Furnace	FF + pre- dedustingDisintegrator/ve nturi scrubber Disintegrator/venturi scrubberESP FF	> <del>99</del> 97 > <del>97</del> 99 > 99.5	23/Mg iron  ∴≤ 5  < 10 for existing plants

# E. Primary and secondary non-ferrous metal industry (annex II, categories 5 and 6)

3639. Smelting processes to obtain non-ferrous metals are known to be large sources of heavy metals released to the atmosphere.<sup>5</sup>

- 40. This section deals with emissions and emission control of Cd, Pbcadmium, lead and Hgmercury in the primary and secondary production of non-ferrous metals like lead, copper, zinc, gold, silver, tin-and, nickel-, manganese and aluminium. Due to the large number of different raw materials used and the various processes applied, nearly all kinds of heavy metals and heavy metal compounds might be emitted from this sector.- Given the heavy metals of concern in this annex guidance document, the production of copper, lead, zinc, gold and zinc manganese production are particularly relevant.
- 37. Mercury ores and concentrates are initially processed by crushing, and sometimes screening. Ore beneficiation techniques are not used extensively, although flotation has been used at some facilities processing low-grade ore. The crushed ore is then heated in either retorts, at small operations, or furnaces, at large operations, to the temperatures at which mercuric sulphide sublimates. The resulting mercury vapour is condensed in a cooling system and collected as mercury metal. Soot from the condensers and settling tanks should be removed, treated with lime and returned to the retort or furnace.
- 38. For efficient recovery of mercury the following techniques can be used:
  - Measures to reduce dust generation during mining and stockpiling, including minimizing the size of stockpiles;
  - Indirect heating of the furnace;
  - Keeping the ore as dry as possible;
  - -Bringing the gas temperature entering the condenser to only 10 to 20°C above the dew point;
  - -Keeping the outlet temperature as low as possible; and
  - -Passing reaction gases through a post condensation scrubber and/or a selenium filter.

Dust formation can be kept down by indirect heating, separate processing of fine grain classes of ore, and control of ore water content. Dust should be removed from the hot reaction gas before it enters the mercury condensation unit with cyclones and/or electrostatic precipitators.

39. For gold production by amalgamation, similar strategies as for mercury can be applied. Gold is also produced using techniques other than amalgamation, and these are considered to be the preferred option for new plants.

<sup>&</sup>lt;sup>5</sup> Pirrone, n. et al, Atmos. Chem. Phys. 10, 5951-5964, (2010); UNEP(DTIE)/Hg/INC.2/4, Study on mercury sources and emissions and analysis of the costs and effectiveness of control measures, November 2010

- 40. Non ferrous metals are mainly produced from sulphitic ores. For technical and product quality reasons, the off-gas must go through a thorough dedusting (< 3 mg/m³) and could also require additional mercury removal before being fed to an SO<sub>3</sub> contact plant, thereby also minimizing heavy metal emissions.

  41. Fabric filters should be used when appropriate. A dust content of less than 10 mg/m³ can be obtained. The dust of all pyrometallurgical production should be recycled in-plant or off-site, while protecting occupational health.
- 42. For primary lead production, first experiences indicate that there are interesting new direct smelting reduction technologies without sintering of the concentrates. These processes are examples of a new generation of direct autogenous lead smelting technologies which pollute less and consume less energy.

  43. Secondary lead is mainly produced from used car and truck batteries, which are dismantled before being charged to the smelting furnace. This BAT should include one melting operation in a short rotary furnace or shaft furnace. Oxy fuel burners can reduce waste gas volume and flue dust production by 60%. Cleaning the flue gas with fabric filters makes it possible to achieve dust concentration levels of 5 mg/m<sup>3</sup>.
- 44. Primary zine production is carried out by means of roast-leach electrowin technology. Pressure leaching may be an alternative to roasting and may be considered as a BAT for new plants depending on the concentrate characteristics. Emissions from pyrometallurgical zine production in Imperial Smelting (IS) furnaces can be minimized by using a double bell furnace top and cleaning with high efficiency scrubbers, efficient evacuation and cleaning of gases from slag and lead easting, and thorough cleaning (< 10 mg/m³) of the CO rich furnace off gases.
- 45. To recover zinc from oxidized residues these are processed in an IS furnace. Very low grade residues and flue dust (e.g. from the steel industry) are first treated in rotary furnaces (Waelz furnaces) in which a high content zinc oxide is manufactured. Metallic materials are recycled through melting in either induction furnaces or furnaces with direct or indirect heating by natural gas or liquid fuels or in vertical New Jersey retorts, in which a large variety of oxidic and metallic secondary material can be recycled. Zinc can also be recovered from lead furnace slags by a slag furning process.

# Table 7 (a): Emission sources, control measures, dust reduction efficiencies and costs for the primary non-ferrous metal industry

- 41. Environmental issues for the production of most non-ferrous metals from primary raw materials, e.g. ores and concentrates, include the emission to air of dust containing heavy metals and metals/metal compounds. Emissions of dust and metals occur from roasters, furnaces, reactors, and the transfer of molten metal. Environmental issues for the production of non-ferrous metals from secondary raw materials, e.g. scrap, residues etc., is also related to the off-gases from the various furnaces and transfers that contain dust and metals.
- 42. In the majority of cases process gases are cleaned in FF. Gas cleaning using wet scrubbers and wet electrostatic precipitators (wet ESP) is particularly effective for process gases that undergo sulphur recovery in a sulphuric acid plant. In some cases where dust is abrasive or difficult to filter, wet scrubbers are also effective. The use of furnace sealing and enclosed transfers and storage is important in preventing diffuse emissions. The significance of diffuse emissions in many processes is very high and diffuse emissions can be much greater than those that are captured and abated. In these cases it is possible to reduce environmental impact by implementing the following measures:
  - (a) Process optimization and minimization of emissions;
  - (b) Sealed reactors and furnaces;
  - (c) Targeted fume collection;
- (d) Use of (mobile) evacuated hood systems above charging, discharging or tapping areas;
  - (e) Closed conveyor routes;

- (f) Unloading and storage of raw materials in closed buildings (or sealed packaging); and
  - (g) Sprinkling systems to avoid emissions from vehicle movements.
- 43. Where prerequisites are given dusts should be recycled internally or externally. BAT for gas collection and abatement for the various process stages regarding to particulate matter (PM) and heavy metals are summarized in the following table:

Table 7 (a)

PM emission control measures for different process stages

Emission source Process Stage	Control measure(s)Measures	Dust reduction efficiency (%)	
Materials handling and storage	Correct storage, handle and fabric filter if necessity		sfer. Dust collection
Grinding, drying	Dust collection and fa	bric filter.	
Roasting/sinteringSintering/roasting, smelting, converting  Conventional smelting (blast furnace reduction)Slag treatment	sintering: ESP + scrubbers (prior to double contact sulphuric acid plant) + FF for tail gasesGas collection and fabric filter, heat recovery, combination of ESP/wet ESP and/or scrubbers.  Shaft furnace: closed top/efficient	<del></del>	<del>7 - 10/Mg</del> H₂SO₄ <del></del>
	evacuation of tap holes + FF, covered launders, double bell furnace topDust collection, cooling and fabric filter.		
Imperial smelting	High-efficiency scrubbing		<del>&gt; 95</del>
Thermal refining	Venturi scrubbersGas collection and fabric filter, combination of ESP/wet ESP and/or scrubbers.	<del></del>	<del></del>
	Double bell furn	ace top	4/Mg metal produced

Emission source Process Stage	Control efficiency measure(s) Measures  Dust Abatement costs (total efficiency costs US\$)
Pressure leaching	Application depends on leaching characteristics of concentrates   site-specific   specific
Direct smelting reduction processes Metal powder production	Flash smelting, e.g. kivcet, Outokumpu and Mitsubishi processGas collection and fabric filter.
Melting and casting	Bath smelting, e.g. top blown rotary converter, Ausmelt, Isasmelt, QSL and Noranda processes Gas collection and fabric filter.  Ausmelt: QSL: operating Pb 77, Cd costs 60/Mg Pb 97; QSL: Pb 92, Cd 93

- 44. In general, processes should be combined with effective PM collecting devices and abatement for both primary gases and diffuse emissions. The BAT associated emission levels for PM are < 1 5 mg/Nm³ using high performance fabric filters or combinations of ESP/wet ESP and scrubbers. In the United States, there are at least thirty control devices at secondary lead smelters that are followed by secondary high efficiency particulate air filter (HEPA) filtration. Many of these thirty HEPA controlled sources are used for controlling building ventilation and process fugitive emissions but some control devices treating furnace exhaust are currently controlled with secondary HEPA filters. PM levels well below 1 mg/Nm³ can be achieved with the combination of certain controls such as a FF plus HEPA filter or FF plus wet ESP6.
- 45. In general emission reduction measures for Pb and Cd are limited to PM abatement whilst emission reduction of Hg requires specific control measures. Table 7(b) below gives examples of PM control costs and Hg reduction efficiencies.
- 46. Table 7 (b): Emission sources, control measures, dust reduction efficiencies and costs for the secondary non-ferrous metal industry

The non-ferrous metals copper, zinc and lead are mainly produced from sulphidic ores. For technical and product quality reasons, the off-gas typically must go through a thorough dedusting ( $< 3 \text{ mg/Nm}^3$ ) and could also require additional mercury (Hg) removal before being fed to an sulphur trioxide ( $SO_3$ ) contact plant, thereby also minimizing heavy metal emissions.

<sup>&</sup>lt;sup>6</sup> U.S. EPA 2010, 2012

Table 7 (b)

Examples of PM control costs and Hg reduction efficiencies 7

Sector	Specific activity indicator (SAI)	Emission control technology	<u>Hg red</u> (%)		nnual costs <sup>a</sup> SD 2008/SAI)	
Emission source	Control measure(s)	Dust reduction efficience y (%)	Abate ment In vest-ment costs (total costs, US\$)	O&M costs	Total costs	
Primary lead						
	metric ton primary lead	Dry ESP	<u>5</u>	<u>0.1</u>	0.04	<u>0.1</u>
	metric ton primary lead	FF	<u>10</u>	<u>0.1</u>	<u>1.1</u>	1.2
	metric ton primary lead	Activated carbon injection +FF+FGD	<u>90</u>	<u>2.5</u>	<u>1.3</u>	<u>3.8</u>
<u>Primary</u> zinc	metric ton primary zinc	<u>Dry ESP</u>	<u>5</u>	0.1	0.06	0.2
	metric ton primary zinc	<u>FF</u>	<u>10</u>	4.5	<u>1.1</u>	<u>5.6</u>
Primary copper	metric ton primary copper	<u>FF</u>	<u>5</u>	1.8	<u>13.8</u>	<u>15.6</u>
Lead production	metric ton primary copper	Short rotary furnace: suction hoods for tap holes + FF; tube condenser, oxy fuel burnerFF state-of-the- art 10	<del>99</del> 3.9-	45/M g Pb-25 .7	29.5	
Zine	<del>Imperial</del>		_	_		
productionSeco ndary lead	ic ton secondary lead	$\begin{array}{ccc} & 14/M \\                                    $	<u>0.1</u>	<u>0.06</u>	<u>0.2</u>	
	metric ton secondary lead	<u>FF</u>	<u>10</u>	<u>6.8</u>	<u>1.1</u>	<u>7.9</u>
Secondary zinc	metric ton secondary zinc	Dry ESP	<u>5</u>	<u>0.1</u>	<u>0.06</u>	0.2

 $<sup>^{7}</sup>$  UNEP(DTIE)/Hg/INC.2/4, Study on mercury sources and emissions and analysis of the costs and effectiveness of control measures, November 2010

<u>Sector</u>	Specific activity indicator (SAI)	Emission control technology	<u>Hg red</u> (%)		nnual costs ' SD 2008/SA	-
Emission source	Control measure(s)	Dust reduction efficience y (%)	Abate ment In vest- ment costs (total costs, US\$)	O&M costs	Total costs	
Secondary copper	metric ton secondary zinc metric ton secondary	<u>FF</u>	<u>10</u>	0.1	<u>1.4</u>	<u>1.5</u>
	copper metric ton secondary	<u>Dry ESP</u>	<u>5</u>	<u>10.9</u>	<u>15.9</u>	<u>26.8</u>
	copper	<u>FF</u>	<u>10</u>	<u>6.6</u>	<u>44.0</u>	<u>50.6</u>

<sup>&</sup>lt;sup>a</sup> The accuracy of cost estimates in the table is within  $\pm$  50 per cent.

- 47. A typical combination of abatement techniques in primary non-ferrous metals production is the use of Dry (Hot) ESP→ water scrubber → Wet ESP→ mercury removal → Sulphuric acid plant. In the case of an acid plant it is desirable to remove the mercury before it enters the acid plant to minimize the possibility that mercury enters the final acid product (normally the quality requirement for Hg in sulphuric acid is < 0.1 ppm (mg/l) which is equivalent to < 0.02 mg/Nm³ in the cleaned gas<sup>8</sup>). Mercury can be treated during both phases the off-gas and the liquid phase (acid plant). Different processes are available. The basic principle is the reaction of mercury with a reagent to form a product which can be precipitated out of the gas or liquid.
- 48. Several technologies for removing mercury vapour from the gas stream are available. The removal efficiency depends on the specific conditions of the gas, e.g. mercury concentration, but can be > 99%. Removal efficiencies for some techniques are given in Table 7(c) below. The following techniques are considered to be BAT:
- (a) The **Boliden Norzink process**<sup>9</sup> is based on the oxidation of mercury vapour by mercuric chloride to form mercurous chloride (calomel) according to the reaction: HgCl<sub>2</sub> + Hg --> Hg<sub>2</sub>Cl<sub>2</sub>. A product acid containing less than 0.5 ppm mercury can be produced from a gas containing 150 ppm mercury (99.7% removal efficiency). The acid produced typically contains 0.3-0.5 ppm of mercury<sup>10</sup>. Mercury can be reduced to 0.05 ppm by adding on a polishing stage with selenium filter<sup>10</sup>. The process is also known as the Outotec chloride scrubber process, the Outotec BN Process and the Odda chloride process. Moderate investment costs and low operating costs, which are practically independent of the mercury level;<sup>12</sup>

<sup>8</sup> Task Force on Heavy Metals post Ottawa background document 2006
http://www.unece.org/fileadmin/DAM/env/lrtap/TaskForce/tfhm/third%20meetingdocs/PostOttawa/B
ackground\_BAT-ELV\_14.06.06.FINAL.doc

<sup>&</sup>lt;sup>9</sup> http://www.sulphuric-acid.com/techmanual/GasCleaning/gcl\_hg.htm

<sup>10</sup> http://www.outotec.com/pages/Page 41301.aspx?epslanguage=EN

- (b) The **Outokumpu process**<sup>9</sup> is based on converting the elemental mercury in the gas into a sulfate according to the reaction:  $Hg + H_2SO_4 --> 1/2 O_2 + HgSO_4 + H_2O$ ;
- (c) The **Bolkem process**<sup>9</sup> is based on mercury being reacted with sulphuric acid and treated with sodium thiosulphate to precipitate the mercury as mercuric sulphide;
- (d) The **selenium filter**<sup>9</sup> is especially suited for low mercury concentrations in the gas and consists of a porous inert material soaked with selenious acid which is then dried to precipitate red amorphous selenium according to the reaction:  $H_2SO_3 + H_2O + 2SO_2 --> Se + 2H_2SO_4$ . The filter will remove approximately 90% of the incoming mercury. The investment cost is proportional to the gas flow rate<sup>6</sup>;
- (e) The **selenium scrubber**<sup>9</sup>, like the selenium filter, relies on the presence of amorphous elemental selenium to react with the elemental mercury in the gas. The selenium scrubber is suitable for removing relative large quantities of mercury in the gas and has a removal efficiency of approximately 90%;
- (f) The activated carbon filter<sup>9</sup> is well known for its adsorption properties. For the adsorption of mercury, activated carbon can normally adsorb 10-12% of its own weight. The operating temperature of the carbon filter is limited to 50°C. The method is especially suitable for low mercury concentrations in the gas. A 90% removal efficiency is normally achievable;
- (g) The **Lurgi application**<sup>11</sup> is a kind of activated carbon filter. Lurgi consists of mercury removal units (MRU) which uses wet ESP and a packed bed absorber using sulphur-impregnated coal to remove mercury from the off-gas. The wet ESP removes dust and tars before the mercury contaminated off-gas is heated to 60-85°C and is absorbed in series of packed bed absorbers. In order to control the gas flow through the unit, the MRU is equipped with a system for pressure control. The MRU has a removal efficiency of 95%;
- (h) The **Tinfos Miltec process**<sup>12</sup> removes mercury from the off-gas by washing it con-currently with seawater containing sodium hypochlorite which oxidizes the mercury. In addition, the wash water collects dust, and reduces sulphur dioxide (SO2) emissions to air. The wash water after gas cleaning contains the mercury as mercury salts, which is added disodium sulfite (Na2S). This leads to the formation of mercury sulfate (HgS) and other metal sulfite precipitate, which can be removed from the process using a press filter. The Miltec process removes 95 % of the mercury from the off-gas;
- (i) The **DOWA filter** process (lead (II) sulfide covered pumice filter) captures metallic, oxidized and particulate mercury.

<sup>&</sup>lt;sup>11</sup> Lurgi GmbH, Eramet Porsgrunn

<sup>12</sup> http://miltec-mercury.com, Eramet Kvinesdal

Mercury removal techniques		$\mu g/Nm^3$	<u>μg/Nm³</u>	Reduction efficiency %
<b>Boliden Norzink Process</b>				
30000 Nm <sup>3</sup> /h	High concentration	<u>9879</u>	<u>30</u>	<u>99.7</u>
	Low concentration	<u>51</u>	<u>13</u>	<u>74</u>
Dowa filter				
170000 Nm <sup>3</sup> /h	High concentration	<u>50</u>	<u>1.4</u>	<u>97</u>
	Low concentration	<u>10.5</u>	<u>1.2</u>	<u>88</u>
Selenium filter				
$80000 \text{ Nm}^3/\text{h}$	High concentration	<u>1008</u>	<u>48</u>	<u>95</u>
	Low concentration	<u>42</u>	<u>12</u>	<u>71</u>
Active carbon filter	High concentration	<u>1206</u>	<u>32</u>	<u>97</u>
80000 Nm <sup>3</sup> /h	Low concentration	<u>37.2</u>	<u>2.7</u>	<u>93</u>

- 49. For processes where mercury removal from the gases is not practicable there are techniques for mercury removal in the liquid phase. These techniques are primarily used to improve the quality of the sulphuric acid. The following techniques to reduce the mercury content in sulphuric acid produced during the production of non-ferrous metals are available:
- (a) Molecular Recognition Technology<sup>9</sup> (MRT) consists of highly selective, often non ion exchange systems using specifically designed ligands or macrocycles. These ligands can be chemically bonded to solid supports such as silica gel or polymers or used free in solution to complex with selected ions. The solid phase system consists of the bound ligand material, called SuperLig, packed into fixed bed columns or filter cartridge elements. The MRT process can be used as the primary method of mercury removal or it can be used as a polishing stage where the plant has an existing mercury removal system;
- (b) The **Toho Process**<sup>9</sup> is based on the addition of potassium iodide and precipitating mercury as mercuric iodide. The addition of cuprous iodide in addition to potassium iodide will form the more stable precipitate Cu<sub>2</sub>HgI<sub>4</sub>. The precipitated mercury is separated by filtration;
- (c) **Sulphide Precipitation**<sup>9</sup>. Colloidal sulphur can be created in the acid by the addition of sodium thiosulphate. The sulphur will react with the mercury to form crystalline mercury sulphide (HgS).
- 50. In the **primary copper** industry the SO<sub>2</sub>-rich primary off-gases from the roasting and converting process are commonly treated in a multi stage abatement plant upstream to

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<sup>&</sup>lt;sup>13</sup> New Boliden, Rönnskärsverken (copper-lead-zinc smelter)

the sulphuric acid plant. In order to produce a high quality sulphuric acid heavy metals need to be reduced (see paras. 46–47). Diffuse emissions occur during charging, discharging, transport and storage processes and from the anode furnace and anode casting process. To avoid these emissions, a sufficient capturing is necessary (see para. 42). After capturing, the loaded off-gas is commonly cleaned in fabric filter systems. If the fabric filter system is well operated and maintained, dust emission concentrations of < 1-5 mg/Nm³ are achievable. For specific heavy metals the following emission concentrations are achievable <sup>14</sup>:

- (a) Lead:  $0.01 0.60 \text{ mg/Nm}^3$ ;
- (b) Cadmium:  $0.01 0.05 \text{ mg/Nm}^3$ ;
- (c) Mercury:  $< 0.01 \text{ mg/Nm}^3$ .
- 51. In the **secondary copper** industry heavy metals emissions occur during smelting, converting and fire refining processes. As in the primary copper industry, the capturing and sufficient treatment of diffuse emissions is crucial (see para. 42). Captured emissions are commonly treated in fabric filter systems. Additionally adsorbent injection, wet scrubbers and/or thermal or regenerative afterburners are used to reduce other pollutants (e.g. SO<sub>2</sub>, TOC or PCDD/F). If the FF system is well operated and maintained dust emission concentrations of < 1-3 mg/Nm³ are achievable. For specific heavy metals the following emission concentrations are achievable <sup>14</sup>:
  - (a) Lead:  $0.01 0.50 \text{ mg/Nm}^3$ ;
  - (b) Cadmium:  $0.01 0.02 \text{ mg/Nm}^3$ ;
  - (c) Mercury:  $< 0.03 \text{ mg/Nm}^3$ ;
- 52. In the **primary lead** industry the  $SO_2$ -rich primary off-gases from the ore oxidation process are commonly treated in a multi stage abatement plant upstream to the sulphuric acid plant. In order to produce a high quality sulphuric acid heavy metals need to be reduced (see paras. 46–47). Diffuse emissions occur during charging, discharging, transport and storage processes and from refining and casting process. To avoid these emissions a sufficient capturing is necessary (see para. 42). After capturing, the loaded off-gas is commonly cleaned in fabric filter systems or in a combination of cyclones and fabric filters. If the fabric filter system is well operated and maintained, dust emission concentrations of  $\leq 1-2$  mg/Nm³ are achievable. For specific heavy metals the following emission concentrations are achievable<sup>14</sup>:
- (a) Lead:  $0.01 0.90 \text{ mg/Nm}^3$ ;
  - (b) Cadmium: 0.01 0.02 mg/Nm<sup>3</sup>;
- (c) Mercury:  $< 0.01 \text{ mg/Nm}^3$ .

53. In general, processes should be combined with an effective dust collecting device for both primary gases and fugitive emissions. The most relevant emission reduction measures are outlined in tables 7 (a) and (b). Dust concentrations below 5 mg/m³ have been achieved in some cases using fabric filters.

#### Cement industry (annex II, category 7)

In the **secondary lead** industry lead acid batteries, residues from batteries and other lead bearing materials are processed. Therefore mercury occurs dependent on the scrapped material. As in the primary lead industry, the capturing and sufficient treatment of diffuse emissions is crucial (see para. 42). After pre-treatment the raw materials are processed in a range of different furnaces. Currently in Europe, Rotary, Blast Drum, and Reverbertaroy

<sup>&</sup>lt;sup>14</sup> UBA Germany 2012, emission values derived from measurements in different German plants

are furnaces used for secondary lead production. Captured emissions are commonly treated in fabric filter systems. By using this technique, dust emission concentrations of 0.5 - 2 mg/m³ are achievable. For specific heavy metals the following emission concentrations are achievable <sup>14</sup>:

- (a) Lead:  $< 0.5 \text{ mg/Nm}^3$ ;
  - (b) Cadmium:  $< 0.05 \text{ mg/Nm}^3$ ;
  - (c) Mercury: 0.025 mg/Nm<sup>3</sup>.15
- 54. In the **primary zinc** industry one has to distinguish between the pyrometallurgical Imperial Smelting Process and the mainly hydrometallurgical process. Only the first process step (roasting) of the hydrometallurgical process creates considerably heavy metals dust in the off-gas. The SO<sub>2</sub>-rich off-gases from the roasting are commonly treated in a multi stage abatement plant upstream to a sulphuric acid plant. In order to produce a high quality sulphuric acid, heavy metals need to be reduced (see paras. 46-47). During the leaching and leach purification steps scrubbers are commonly used to clean the occurring off-gases. By using these techniques, dust emission concentrations of 0.3 1 mg/Nm³ are achievable. For specific heavy metals the following emission concentrations are achievable achievable.
  - (a) Lead:  $< 0.01 \text{ mg/Nm}^3$ ;
  - (b) Cadmium: < 0.01 mg/Nm<sup>3</sup>;
- (c) Mercury: mainly removed in wet process steps, measured after waste water  $\frac{\text{treatment plant:}}{\text{treatment plant:}} < 0.005 \text{ mg/l.}$
- 55. Cadmium is a by-product in the primary zinc industry. It is produced in a separate four stage process:
  - (a) Smelting of cadmium briquettes from leach cleaning process;
  - (b) Dezincification with caustic soda;
  - (c) Vacuum distillation to separate cadmium from other metals like Cu, Ni, Pb;
- (d) Condensation in fine-cadmium furnace and casting. The off-gases from furnaces are commonly captured and treated in an advanced ESP. By using this technique, dust emission concentrations of 0.3 1 mg/Nm³ are achievable. For specific heavy metals the following emission concentrations are achievable <sup>14</sup>:
- (e) Lead:  $< 0.01 \text{ mg/Nm}^3$ ;
  - (f) Cadmium:  $< 0.01 \text{ mg/Nm}^3$ .

To avoid diffuse emissions sufficient capturing and treatment is necessary (see para. 42).

56. **Secondary zinc** can be produced from EAF-dust and other zinc bearing materials. These materials can be refined in rotary furnaces (Waelz process) to separate the zinc from other elements. In this process, heavy metals occur as dusty emissions which are mainly captured and treated in multi stage fabric filter systems. To reduce gaseous mercury emissions it is common to inject an adsorbent (lime, activated coke etc.) into the off-gas stream before the last fabric filter step. By using these techniques, dust emission concentrations of 0.5 - 5 mg/Nm³ are achievable. For specific heavy metals the following emission concentrations are achievable  $^{14}$ :

<sup>&</sup>lt;sup>15</sup> Environment Agency Austria (UBA) 2003, emission value derived from measurement in an <u>Austrian plant</u>

- (a) Lead:  $< 0.02 \text{ mg/Nm}^3$ ;
- (b) Cadmium:  $< 0.01 \text{ mg/Nm}^3$ ;
- (c) Mercury:  $< 0.01 0.05 \text{ mg/Nm}^3$ .

To avoid diffuse emissions, a sufficient capturing and treatment is necessary (see para. 42).

- 57. For large-scale gold production various alternative processes to amalgamation have been developed. In cases where mercury levels in various ores are elevated (e.g. dome gold mine ores) activated carbon adsorber beds can be used to capture most of the mercury emissions from various processes (e.g. kilns, refinery furnaces). By applying pollution prevention measures, including mercury condensers, carbon adsorption units (e.g., single fixed carbon beds, multiple beds or columns or other designs), mercurous chloride scrubbers, venturi scrubbers, and chemical additives to improve mercury capture, mercury emissions from gold production have been reduced by about 97%<sup>16</sup>.
- 58. **Manganese production** from ore with high content of mercury is a significant source of mercury emissions. Using activated carbon adsorption of mercury in waste gas from furnace can give reductions of 95%.

#### F. Cement industry

- 59. Cement kilns may use secondary fuels and materials (waste co-processing) such as waste oil or waste tyres. Where waste is used, emission requirements for waste The co-incineration processes may apply, and where hazardous waste is used waste in cement kilns is treated within the waste incineration category. Mercury emissions can be reduced by controlling the amount of mercury in the input of the kiln, reducing the off-gas temperature to improve mercury precipitation during first filtration or by abating mercury through activated carbon injection as an adsorbent to the flue-gas. Quality control of fuels and content of mercury of raw materials should be checked in order to reduce and limit mercury emissions.
- Mercury and its compounds are not completely precipitated and retained in the kiln system and/or the pre-heater due to the high temperatures existent there and the mercury high volatility. They are precipitated on the exhaust gas route due to the cooling of the gas and are partially adsorbed by the raw material particles, depending on the amount used in the plant, emission requirements for hazardous waste incineration processes may apply. However, this section refers to fossil fuel fired kilnstemperature of the exhausted gas. This portion is precipitated in the kiln exhaust gas filter. Therefore, mercury may only become enriched in the external cycle, where the concentration level and the emissions are mainly determined by the exhaust gas conditions. To prevent a long-cycle increase in mercury emissions, it may become necessary to limit the concentration of the external cycle, e.g. by continuously or intermittently extracting part of the dust collected in the filter system. The dust from the dust collector can be recirculated back to the cement mill. Furthermore, precipitation and hence, mercury removal increases with decreasing exhaust gas temperature. Therefore, another possibility to reduce mercury emissions is to reduce the off-gas temperature after the conditioning tower to improve the precipitation of mercury and its compounds during dust filtration.

<sup>&</sup>lt;sup>16</sup> U.S. EPA; National Emission Standards for Hazardous Air Pollutants: Gold Mine Ore Processing (EPA-HO-OAR 2010-0239; FRL-9242-3)

- 48. Particulates are 61. Dust is emitted at all stages of the cement production process, consisting of material handling, raw material preparation (crushers, dryers), clinker production and cement preparation. Heavy metals are brought into the cement kiln with the raw materials, fossil and waste fuels Mercury is predominantly introduced into the kiln with raw-materials with generally a minor amount coming from the fuels. There is a constant increase in the use of waste fuels in the clinker production, which can be a source of heavy metals. It is generally the raw material input and not the process type which has the greater effect on heavy metal emissions.
- 4962. For clinker production the following kiln types are available: long wet rotary kiln, long dry rotary kiln, rotary kiln with cyclone preheater, rotary kiln with cyclone pre-heater, rotary kiln with grate preheater, pre-heater, long wet rotary kiln, long dry rotary kiln and shaft furnace. In terms of The selected process has a major impact on the energy demand and emission control opportunities, rotary kilns with eyelone preheaters are preferable use and air emissions from the manufacture of cement clinker. For new plants and major upgrades the best available technique for the production of cement clinker is considered to be a dry process kiln with multi-stage preheating and precalcination.
- 5063. For heat recovery purposes, rotary kiln off-gases are conducted through the preheating system and the mill dryers (where installed) before being dedusted.— The collected dust is returned to the feed material. Excess heat from the kiln off-gases as well as from the clinker cooler can be used for electricity generation (cogeneration) or externally, e.g. for district heating.
- 5164. Less than 0.5% of lead and cadmium entering the kiln is released in exhaust gases. The high alkali content and the scrubbing action in the kiln favour metal retention in the clinker or kiln dust.
- 5265. The emissions of heavy metals into the air can be reduced by, for instance, taking off a bleed stream and stockpiling the collected dust instead of returning it to the raw feed. However, in each case these considerations should be weighed against the consequences of releasing the heavy metals into the waste stockpile. Another possibility is the hot meal bypass, where calcined hot meal is in part discharged right in front of the kiln entrance and fed The collected dust can be recirculated also to the cement preparation plant. Alternatively, the dust can be added to the clinker. Another mill. If the exhaust gas of the kiln is filtered by ESPs, an important measure is to have a very well controlled steady operation of the kiln in order to avoid emergency shut-offs of the electrostatic precipitators. ESPs. These may be caused by excessive CO concentrations. It is important to avoid high peaks of heavy metal emissions in the event of such an emergency shut-off. BAT for the manufacturing of cement with regard to dust and heavy metals emissions the combination of the following general primary measures:
- (a) A smooth and stable kiln process. Therefore to carry out monitoring and measurement of process parameters and emissions on a regular basis is important;
- (b) Careful selection and control of substances entering the kiln; if available selection of raw materials and fuels with low contents of sulphur, nitrogen, chlorine, metals (especially mercury) and volatile organic compounds should be preferred;
- (c) Use of a quality assurance system to control the characteristics of wastes to be used as raw material and/ or fuel for constant quality and other physical and chemical criteria. Relevant parameters for any waste to be used as raw material and/or fuel should be controlled;

(d) Use of effective dust removal measures/ techniques like fabric filters (with multiple compartments and 'burst bag detectors') or ESP (with fast measuring and control equipment to minimize the number of carbon monoxide trips);

To minimize/ reduce dust emissions from *diffuse sources*<sup>17</sup> the following measures and techniques can be used:

- (e) Minimization/prevention of dust emissions from diffuse sources;
- (f) Measure techniques for dusty operations;
- (g) Bulk storage area measures/ techniques.

<u>66.53.</u> The most relevant emission reduction measures are outlined in table 8.- To reduce direct dust emissions from crushers, mills, and dryers, <u>fabric filters FF</u> are mainly used, whereas kiln and clinker cooler waste gases are controlled by <u>electrostatic precipitators</u>. With ESP, <u>dustESP</u> or FF. Dust emissions from kiln firing processes, <u>cooling and milling processes</u> can be reduced to concentrations <u>below 50< 10 - 20</u> mg/m<sup>3</sup>. When FF are used, the clean gas dust content can be reduced to  $Nm^3$  (daily mean value, 10 vol%  $O_2$ ), from other processes to concentrations < 10 mg/m<sup>3</sup>- $Nm^3$ .

Table 8: Emission sources, control measures, reduction efficiencies and costs for the cement industry

Emission source	Control measure(s)	Reduction efficiency (%)	Abatement costs Reported emissions (mg/Nm³)
Direct emissions from crushers, mills, dryerskiln firing, cooling and milling processes	FF Primary measures plus FF or ESP	Cd-, Pb: > 95-	Dust: < 10 – 20
Direct emissions from rotary kilns, clinker coolers dusty operations 18	ESP Primary measures plus FF or ESP	Cd. Pb: > 95	<u>Dust&lt; 10</u>
Direct emissions from rotary kilns	Carbon Activated carbon adsorption-	Hg: > 95-	Hg: 0.001 – 0.003

# Glass industry (annex II, category 8)

67. A way to minimize mercury emissions is to lower the exhaust temperature. When high concentrations of volatile metals (especially mercury) occur, adsorption on activated carbon is an option; an increased efficiency of ESP could be shown when using additionally halogenides (especially bromides).

<sup>&</sup>lt;sup>17</sup> Detailed description of measures for diffuse sources in chapters 1.4.4.1 and 1.4.4.3 of the Best available techniques reference document (BREF) for Cement, Lime and Magnesium Oxide Manufacturing Industries http://eippcb.jrc.ec.europa.eu/reference/BREF/clm\_bref\_0510.pdf
<sup>18</sup> Dusty operations: e.g. crushing of raw material, conveyers and elevators, storage of fuels and raw material

#### G. Glass industry

68. In the glass industry, lead emissions are particularly relevant given the various types of glass in which lead is introduced as raw material—(e.g. crystal glass, cathode ray tubes). Lead is used in fluxes and colouring agents in the frit industry, in some special glasses (e.g. coloured glasses, cathode ray tube (CRT) funnels) and domestic glass products (lead crystal glasses). In the case of soda-lime container glass, lead emissions depend on the quality of the recycled glass used in the process.—External cullet is an important source of metal contamination particularly for lead. The lead content in dusts from crystal glass melting is usually about 20-60%.—80%.

5569. Dust emissions stem mainly from batch mixing, furnaces, diffuse leakages from furnace openings, and finishing and blasting of glass products.- They depend notably on the type of fuel used, the furnace type and the type of glass produced.- Oxy-fuel burners can reduce waste gas volume and flue dust production by 60%.- The lead emissions from electrical heating are considerably lower than from oil/gas-firing. In general and where it is economically viable, predominantly electrical melting is considered BAT for lead crystal, crystal glass and opal glass production, since this technique allows efficient control of potential emissions of volatile elements. Where crystal glass is produced with a less volatile formulation, other techniques may be considered when determining BAT for a particular installation.

5670. The batch is melted in continuous tanks or crucibles. During the melting cycle using discontinuous furnaces, the dust emission varies greatly. The dust emissions from crystal glass tanks ( $<_5$ -kg/Mg melted glass) are higher than from other tanks ( $<_1$ -kg/Mg melted soda and potash glass). BAT for lead from the melting furnace in the domestic glass sector when used for manufacturing lead crystal glass is <0.5-1 mg/Nm³ (<0.001-0.003 kg/t melted glass).

- 5771. Some measures to reduce direct metal-containing dust emissions are: pelleting
  - (a) Pelleting the glass batch, changing;
- (b) Changing the heating system from oil/gas-firing to electrical heating; eharging;
  - (c) Charging a larger share of glass returns (cullet) in the batch, and applying;
- (d) Applying a better selection of raw materials (size distribution) and recycled glass (avoiding lead-containing fractions). Exhaust gases can be cleaned in fabric filters, reducing the emissions below 10 mg/m<sup>3</sup>. With electrostatic precipitators 30 mg/m3 is achieved. The corresponding emission reduction efficiencies are given in table 9.

58In general, BAT for controlling dust emissions from furnaces in the glass industry is the use of either an ESP or FF system, operating where appropriate, in conjunction with a dry or semi-dry acid gas scrubbing system. The BAT emission level for dust associated with these techniques is generally < 10 – 20 mg/Nm³, for some glass types such as domestic glass or special glass generally < 10 – 20 mg/Nm³ and 1 - 10 mg/Nm³, when significant amounts of dangerous substances are applied which generally equates to less than 0.1 kg/tonne of glass melted. In some cases, the application of BAT for metals emissions may result in lower emission levels for dust. The emission level associated with BAT for the sum of the concentrations of heavy metals including lead (As, Co, Ni, Cd, Se, Cr, Sb, Pb, Cu, Mn, V, Sn) is generally < 1 - 5 mg/Nm³. Secondary dust abatement represents BAT for most glass furnaces, unless equivalent emissions can be achieved with primary measures. The corresponding emission reduction efficiencies are given in table 9.

- <u>72</u>. The development of crystal glass without lead compounds is in progress. <u>The Plasma Melter makes use of the electrical conductivity of molten glass and operates with negligible dust emissions. It is however not expected to be a viable technique for melting within the foreseeable future.</u>
- 73. For potentially dusty downstream activities BAT is considered to be dust minimization, e.g. by cutting, grinding or polishing under liquid or by extraction of off gases to a bag filter system. The emission level for these activities is < 1 10mg/Nm³ (up to 20 mg/Nm³ for flat glass and up to 50 mg/Nm³ only for mineral wool downstream processes).

Table 9:-Emission sources, control measures, dust reduction efficiencies and costs for the glass industry

Emission source	Control measure(s)	Dust reduction– efficiency (%)	Abatement costs (total costs)
Direct emissions	FF	> <mark>98</mark> _ <u>99</u>	<del></del>
-	ESP	> <del>90</del> ~ <u>95</u>	<del></del>

# <u>H.</u>Chlor-alkali industry (<del>annex II, category 9)</del>

5974. In the chlor-alkali industry, chlorine gas ( $Cl_{27}$ ), alkali hydroxides and hydrogen are produced through electrolysis of a salt solution.- Commonly used in existing plants are the mercury process-and, the diaphragm process, both of which and the membrane process. All these processes need the introduction of good practices to avoid reduce environmental membrane process results in no direct mercury problems.emissions. Moreover, it shows a lower electrolytic selected process technology has a major impact on the energy use and higher heat demand for emissions from the manufacture of chlor-alkali hydroxide concentration (the global energy balance resulting in a slight advantage for. BAT for the production of chlor-alkali is considered to be membrane technology. Non-asbestos diaphragm technology can also be considered as BAT. The use of mercury-cell technology in the range of 10 to 15%) has been declining in Europe and a more compact cell operation. It is, therefore, considered as the preferred option for new North America over the past few decades, as many such plants- have shut down or been converted to non-mercury processes. Moreover, European and North American producers are committed to not building any new mercury-cell facilities. The last chlor-alkali mercury cell plant in Canada closed in 2008. European regulations do not allow the construction of these facilities.

75. Mercury releases from chlor-alkali operations can be entirely eliminated only by converting to a non-mercury process such as the membrane cell process. Conversion to membrane cell technology is considered as BAT. Decision 90/3 of 14 June 1990 of the Commission for the Prevention of Marine Pollution from Land-based Sources (PARCOM) recommends that existing mercury cell chlor-alkali plants should be phased out as soon as practicable with the objective of phasing them out completely by 2010. The Decision 90/3 was reviewed in 1999-2001 without any changes. Among countries of the Oslo and Paris Conventions for the protection of the marine environment of the North-East Atlantic (OSPARCOM) and in the European Union there has been considerable discussion about the

possible impacts the re-marketing of the mercury from decommissioned chlor-alkali facilities will have on the global mercury market. In 1999 all West European chlor-alkali producers presented the authorities with a voluntary commitment to shut down their chlor-alkali plants by 2020 latest. Another clause of the PARCOM Decision 90/3 commits them not to sell or transfer mercury cells after plant shutdown to any third party for re-use. In February 2009, the Governing Council of UNEP agreed on the need to develop a global legally binding instrument on mercury and started negotiations of a global mercury convention. Key elements of these negotiations are, for example, reducing the supply of mercury onto the market, reducing mercury demand for products and processes, reducing atmospheric emissions of mercury, addressing mercury containing waste and remediation of contaminated sites. The negotiations shall be finished by 2013.

- 6076. The specific investment for replacing mercury cells by the membrane process is reported to be in the region of US\$ 700-1000/Mg Cl<sub>2</sub> capacity.- Although additional costs may result from, inter alia, higher utility costs and brine purification cost, the operating cost will in most cases decrease.- This is due to savings mainly from lower energy consumption, and lower waste-water treatment and waste-disposal costs.
- 61.-77. The sources of mercury emissions into the environment in the mercury process are: cell room ventilation; process exhausts; products, particularly, end box ventilation air and by-product hydrogen; and waste water. With regard to emissions into air, Hg diffusely emitted from the cells to the cell room are particularly relevant. Preventive measures and control are of great importance and should be prioritized according to the relative importance of each source at a particular installation. In any case specific control measures are required when mercury is recovered from sludges resulting from the process.
- 62. The following measures can be taken to reduce emissions from existing mercury process plants:
  - Process control and technical measures to optimize cell operation, maintenance and more efficient working methods;
  - -Coverings, sealings and controlled bleeding off by suction;
  - -Cleaning of cell rooms and measures that make it easier to keep them clean; and
  - Cleaning of limited gas streams (certain contaminated air streams and hydrogen gas).

    63.78. During the remaining life of mercury cell plants, all possible measures should
    - be taken to protect the environment as a whole, including minimizing mercury losses to air by:
    - (a) Use of equipment and materials and, when possible, a lay-out of the plant that minimizes losses of mercury due to evaporation and/or spillage;
      - (b) Good housekeeping practices and good maintenance routines;
    - (c) Collection and treatment of mercury-containing gas streams from all possible sources, including hydrogen gas. Typical devices for removal of mercury air emissions are shown in table 10 (a):
      - (d) Reduction of mercury levels in caustic soda;
    - (e) Minimizing current and future mercury emissions from handling, storage, treatment and disposal of mercury-contaminated wastes;
    - (f) Decommissioning carried out in a way that prevents environmental impact during and after the shutdown process as well as safeguarding human health.

#### Table 10 (a)

### Control measures, reduction efficiencies and costs for chlor alkali plants emissions

Emission source	<u>Control measure</u>	Reduction efficiency
Chlor-alkali production	Gas stream cooling to remove mercury from hydrogen stream; mist eliminators;	
	scrubbers;  adsorption on activated carbon and molecular sieves.	> <u>90</u>

79. These measures can cut mercury emissions to values well below 2.0 g/Mg of Cl<sub>2</sub>-production capacity, expressed as an annual average. There are examples of plants that achieve emissions well below 1.0 g/Mg of Cl<sub>2</sub> production capacity. As a result of PARCOM decision 90/3, existing mercury based chlor alkali plants were required to meet the level All plants comply with the limit value of 2 g of Hg/Mg Cl<sub>2</sub> for air emissions in PARCOM Decision 90/3, and it is clear that in many plants, air emissions continue to fall. However, for reported emissions a wide range in actual values from 0.14 to 1.57 g Hg/Mg of Cl<sub>2</sub> by 31 December 1996 for emissions covered by the Convention for the Prevention of Marine Pollution from Land-based Sources. is shown. The best performing mercury cell plants are achieving total mercury losses to air, water and with products in the range of 0.2 – 0.5 g Hg/Mg Cl<sub>2</sub> as a yearly average, and with regard to air emissions 0.21 – 0.32 g Hg/Mg Cl<sub>2</sub>, as shown in table 10 (b). Since emissions depend to a large extent on good operating practices, the average should depend on and include maintenance periods of one year or less.

Table 10 (b)

#### Mercury losses to air from best performing mercury cell plants

	g Hg/Mg Cl <sub>2</sub> <sup>19</sup>
Cell room	0.2 - 0.3
Process exhausts, including Hg distillation unit	0.0003 - 0.01
Untreated cooling air from Hg distillation unit	0.006 - 0.1
Hydrogen gas	< 0.003

# Municipal, medical and hazardous waste incineration (annex II, categories 10

80. There are wastes that are neither classified as hazardous, municipal or medical wastes, depending on national legislation (e.g. non-hazardous industrial wastes, sludge etc.), that may be incinerated as well as co-incinerated in other industries, therefore potentially constituting a relevant source of heavy metal emissions. Furthermore, there are other thermal waste treatment methods (e.g. pyrolysis) that may be a relevant source of heavy metal emissions. For BAT, no differentiation is made between municipal, hazardous and 11)

64. —medical waste in terms of applied techniques or achievable emission limits, as all types of waste are often incinerated in the same installation. Emissions of cadmium, lead and mercury result from the incineration of municipal, medical and hazardous waste.- Mercury, a substantial part of cadmium and

<sup>&</sup>lt;sup>19</sup> Total grams of mercury per megagramme of chlorine production.

minor parts of lead are volatilized in the process.- Particular actions should be taken both before and after incineration to reduce these emissions.

65. The best available technology only relevant primary techniques for preventing emissions of mercury into the air before incinerating are those that prevent or control, if possible, the inclusion of mercury in waste. In some countries mercury-containing components are separated out of the solid waste stream and managed or recycled properly. Removing mercury from the waste stream before it enters the incinerator is much more cost-effective than capturing mercury later from flue gases using emissions control devices. Lower emissions of mercury from municipal waste combustors and medical waste incinerators can be achieved through product substitution. Although this is potentially applicable to a wide range of components, batteries have received the greatest attention because of their significant contribution to total mercury content in municipal and medical wastes. The applicability of the product substitution to other areas should be based on technical and economic feasibility.

81. The BAT for dedusting and reducing heavy metals emissions is considered to be fabric filters—FFs in combination with dry or wet methods for controlling volatiles. Electrostatic precipitators ESPs in combination with wet systems can also be designed to reach low dust emissions, but they offer fewer opportunities than fabric filters FFs especially with pre-coating for adsorption of volatile pollutants. Between 30 % and 60 % of mercury is retained by high efficiency ESPs or FFs and flue gas desulphurization (FGD) systems capture further 10 to 20%. When using dry system, the additional injection of activated carbon (impregnated with sorbents like sulphur, bromine or others), sodium hydrogen carbonate or calcium hydroxide upstream of a fabric filter or use of lignite coke or zeolite can reduce the mercury emissions by more than 90%. When using a wet scrubber system with ESP or FF, to improve the mercury removal different chemicals can be added to the wet scrubber solution, e.g. hydrogen peroxide, liquid chelating reagents with copper or manganese salts or sodium hypochlorite (NaClO).

66.82. When BAT is used for cleaning the flue gases, the concentration of dust willcan be reduced to a range of 10 to 20 mg/m³; in practice 1 – 5 mg/m³. In general, the use of fabric filters gives the lower concentrations are reached, and in some cases concentrations of less than 1 mg/m³ have been reported. levels within these emission ranges. Effective maintenance of dust control systems is very important. Controlling dust levels generally reduces metal emissions too. The concentration of mercury can be reduced to a range of 0.05 to 001 – 0.10 02 mg/m³ (m³ (daily average, normalized to 11% O<sub>2</sub>). Adsorption using carbon based reagents is generally required to achieve these emission levels with many wastes. Some waste streams have very highly variable Hg concentrations and waste pre-treatment may be required in such cases to prevent peak overloading of FGT system capacity.

67.-83. The most relevant secondary emission reduction measures are outlined in table-10.- It is difficult to provide generally valid data because the relative costs in US\$/tonne depend on a particularly wide range of site-specific variables, such as waste composition.

68. Heavy metals are found in all fractions of the municipal waste stream (e.g. products, paper, organic materials). Therefore, by reducing the quantity of municipal waste that is incinerated, heavy metal emissions can be reduced. This can be accomplished through various waste management strategies, including recycling programmes and the composting of organic materials. In addition, some UNECE countries allow municipal waste to be landfilled. In a properly managed landfill, emissions of cadmium and lead are eliminated and mercury emissions may be lower than with incineration. Research on emissions of mercury from landfills is taking place in several UNECE countries.

Table 10: Emission sources, control measures, reduction efficiencies and costs for municipal, medical and hazardous waste incineration

- 84. If re-burn of flue gas treatment residues is applied, then suitable measures should be taken to avoid the re-circulation and accumulation of Hg in the installation.
- 85. Metallic mercury can be adsorbed (usually at about 95% removal efficiency) to result in emissions to air of below 30  $\mu$ g/Nm³ if an activated carbon injection in combination with a de-dusting device is used. Ionic mercury is also removed by chemi-adsorption due to the sulphur content in the flue-gases or from sulphur impregnated carbon in some types of activated carbon. There is a significant fire risk when using activated carbon. The adsorbent may be mixed with other reagents to reduce the fire risk. 90% lime and 10% carbon is used in some cases. The proportion of carbon is generally higher where there are additional process stages that perform acid gas removal (e.g. wet scrubbers) In some systems where removal of mercury is carried out in wet acid scrubbers (pH < 1) to reduce the inlet concentration, final emission levels below 1  $\mu$ g/Nm³ are seen.
- 86. Selective catalytic reduction (SCR) for control of nitrogen oxides also reduces mercury emissions as a co-benefit by changing it into a form that can be collected by FF or precipitated by wet scrubbers.
- 87. Most Parties require discontinuous monitoring of mercury emissions only, while some consider continuous monitoring as BAT; proven systems for continuous measurements of mercury emissions are available on the market.
- 88. For the co-incineration of waste and recovered fuel in cement kilns, in general, the BAT for cement kilns apply.
- 89. For the co-incineration of waste and recovered fuel in combustion installations, in general, the BAT for combustion installations apply.
- 90. The PECK process is a promising technique with negligible heavy metals emissions in the flue gas. It has been developed for municipal solid waste treatment but could in principle be applied to other wastes. Other options to reduce heavy metals emissions may be the heavy metal evaporation process and the hydro-metallurgical treatment plus vitrification.
- 91. If the first stage of a high efficiency scrubber is kept at a pH of below 1, the removal efficiency of ionic Hg as  $Hg_2Cl_2$ , which is generally the main compound of mercury after waste combustion, is over 95%. Metallic mercury adsorption can be improved by addition of sulphur compounds to the scrubber liquor or addition of activated carbon to the scrubber liquor or addition of oxidants, e.g. hydrogen peroxide to scrubber liquor. The overall Hg removal (both metallic and ionic) efficiency is around 85%. Achieved levels just with a wet scrubbing system are approximately  $36 \, \mu g/Nm^3$ , with a wet scrubber and an activated coke filter  $< 2 \, \mu g/Nm^3$  and with a combination of the flow injection process and a wet scrubber  $4 \, \mu g/Nm^3$ .

Table 11
Control measures, dust reduction efficiencies and costs for municipal, medical and hazardous waste incineration for stack gases

Emission source	Control measure(s)	Reduction efficiency (%)	Abatement costs (total costs US\$)
Stack gases	High-efficiency scrubbers	Pd, Cd: > 98; Hg: ca. 50	
	ESP (3 fields) with activated carbon or equivalent adsorptive	Pb, Cd <u>+:</u> 80 <u>-</u> _	10-20/Mg waste

Emission source	Control measure(s)	Reduction efficiency (%)	Abatement costs (total costs US\$)
	reagents  Wet ESP (1 field) with additives, in combination with activated carbon injection, or activated carbon or coke filters	Pb, Cd: 95 99 <u>Hg: &gt; 90</u> (1μg/Nm3)	1,600 − 4,000 per pound Hg removed
	Fabric filters	Pb, Cd: 95 99	15-30/Mg waste
	Activated Carbon injection + FF or ESP	Hg: > 8550 – 95 (< 1 μg/Nm3)	operating costs; ca. 2-3/MewasteOperating costs: ca. 2-3/Mgwaste; MWCs 211 - 870; Medical Waste Incinerators, 2,000 - 4000 per pound Hgremoved. Operating cost (carbor cost): EUR 125000/a for a facility treating 65.000 tons of hazardous waste <sup>20</sup>
	Carbon bed filtration	Hg: > 99	operatingOperating costs:: ca. 50/Mg waste: 513 – 1,083 per pound Hg removed
	Selenium filters (inlet mercury concentrations of up to 9 mg/m³)		

# J. Waste containing metallic mercury and certain mercury compounds and mixtures

[92. In global artisanal and small-scale gold mining yearly more than 1000 tonnes of mercury are used of which over 500 tonnes are emitted to air. This is two times more than the total emission to air in 2008 from the European Monitoring and Evaluation Programme (EMEP) territory. Although these emissions take place in developing countries, emissions undergo long-range transboundary transport and thus affect health and environment in the United Nations Economic Commission for Europe (ECE) territory. In this context export of mercury from Europe is very relevant.]

[93. Europe alone exported in 2008 1300 tonnes of mercury a year, while worldwide trade amounted to 2200 tonnes. Mercury in use and in stock is much bigger than the mercury traded globally. In the 27 European Union countries, Norway and Switzerland 34,000 tonnes of mercury were in stock. Most of this is linked to the chlor-alkali industry where industry will abandon the mercury electrolysis process. It is estimated that in 2008

<sup>&</sup>lt;sup>20</sup> BREF Waste Incineration, chapter 4.4.6.2 (2006), http://eippcb.jrc.es/reference/wi.html

mercury waste from chlor-alkali plants was between 12 and 20 t/year (with an average of 18 t).<sup>21</sup>

[94. UNEP advises countries to ban the export of mercury and to dispose of mercury containing waste in an environmental sound manner. As a result the supply will go down and the prices will be likely to go up. The price of mercury on the global market is currently slowly decreasing and lies in the range of 4-20 US\$ per kilogramme. Norway and the European Union have in 2011 instituted a general prohibition on export, sale and use of mercury and mercury compounds. They also have regulations on the safe disposal of mercury waste. The U.S. has banned the export of elemental mercury from 2013 onwards and has created an obligation for the administration to provide for a facility for safe storage by 2013. The disposal costs have been calculated at 0.5 US\$ per kilogramme.]

[95. The following should be considered as waste and should be disposed of in an environmentally sound manner, taking into account relevant sub-regional, regional and global regimes governing the management of hazardous wastes and their disposal, in particular the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal:

- (a) Metallic mercury that is no longer used in the chlor-alkali industry;
- (b) Metallic mercury resulting from the cleaning of natural gas;
- (c) Metallic mercury and mercury compounds resulting from the cleaning of exhaust gasses of stationary sources;
  - (d) Metallic mercury resulting from non-ferrous mining and smelting operations;
  - (e) Metallic mercury extracted from cinnabar ore; and
  - (f) Obsolete mercury-containing products.]

[96. The disposal of mercury-containing waste and the transboundary movement of waste should be carried out in an environmentally sound manner, taking into consideration applicable sub-regional, regional and global regimes governing the transboundary movement and the management of hazardous wastes and their disposal, in particular the Basel Convention and its Technical Guidelines for the Environmentally Sound Management of Wastes Consisting of Elemental Mercury and Wastes Containing or Contaminated with Mercury.]

<sup>&</sup>lt;sup>21</sup> Pirone, N. et al; Global mercury emissions to the atmosphere from antropogenic and natural sources; Atmos.Chem.Phys.,10, 5951-5964